

PATENT ABSTRACTS OF JAPAN

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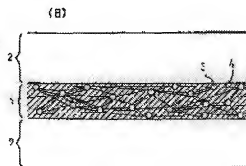
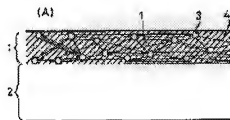
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(54) POLYMER SOLID ELECTROLYTE-ELECTRODE JOINED BODY

(57)Abstract:

PURPOSE: To improve the energy efficiency and current density of an electrochemical device using a polymer solid electrolyte by integrally forming the polymer solid electrolyte adding a solid electrolytic resin contained in the porous void part of a drawn porous polytetrafluoroethylene (PTFE) on the surface of an electrode.

CONSTITUTION: A polymer solid electrolyte 1 formed of a drawn porous polytetrafluoroethylene (PTFE) and a polymer solid electrolytic resin contained in its porous void part is integrally formed on the surface of an electrode 2, whereby a polymer solid electrolyte-electrode joined body is provided. When the polymer solid electrolytic resin solution is applied onto the electrode surface to form a film, for example, the drawn porous PTFE film is preliminarily arranged on the electrode surface. Thus, most of the resin component is contained in the void part of the drawn porous PTFE, and the resin partially penetrated into the reverse side contributes to the junction as a binder with the electrode.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a solid polymer electrolyte and an electrode conjugate. Although it can use for the water electrolysis system etc. which use the lithium cell or proton conductivity solid electrolyte which uses a lithium ion conductive solid electrolyte in more detail with respect to the electrode and solid polymer electrolyte zygote of the electrochemical device which uses an ion conductivity solid polymer electrolyte, It is used for the polymers solid oxide fuel cell which uses a proton conductivity solid electrolyte the optimal.

[0002]

[Description of the Prior Art]Much more improvement in energy efficiency is called for, therefore electrode structure is devised, three-dimensions-ize an electrode reaction point, and it is made to increase a labile point, and a solid polymer electrolyte is arranged also inside an electrode, and it enables it to move ion promptly in the electrochemical device which uses a solid polymer electrolyte. In order to be able to move promptly the ion by which it was generated to a counter electrode, contact with the solid electrolyte in an electrode and the solid-electrolyte membrane which is barrier membrane needs to be good, and the membrane resistance of the solid-electrolyte membrane itself needs to be low, and, for that purpose, the thinner possible one of thickness is preferred. If the polymers solid-electrolyte membrane currently used with the fuel cell always is not used by a damp or wet condition, humidify to reactant gas, and are trying to maintain a damp or wet condition indirectly, since polarization occurs and performance falls, an ion-conductive fall and, but. A humidity effect is so good that a polymers solid-electrolyte membrane is thin, and improvement in limiting current density can be expected.

[0003]After preparing a solid-electrolyte membrane and an electrode for according to, respectively and piling these up conventionally, the method of joining with a hotpress is

generally performed.

What was fabricated in the shape of a film as a commercial item as a solid polymer electrolyte (for example, U.S. Du Pont make Nafion #115 grade), the thing which carried out the cast of the solution and fabricated it filmy, etc. are used.

Using it, inserting mechanically, without carrying out a hotpress is also proposed.

[0004]

[Problem(s) to be Solved by the Invention]However, in junction by a hotpress, since a pressure was applied in the place which the film softened with temperature, when thickness was made not much thin, the film was destroyed, and there was a problem of having produced gas leakage or being easy to generate an inter-electrode short circuit. Since this posed a still more difficult problem when the smooth nature of an electrode is bad, it was difficult to make thickness thin extremely. There were also the electrode itself and a problem of spoiling the breathability which is an element whose electrode for enabling the operation with high current density is important since a consolidation is carried out, at the time of a hotpress.

[0005]Although I hear that problems, such as these, are solved and the hot pressing step itself can be skipped and the method of using it, inserting mechanically is also proposed, In order to keep low keeping contact with an electrode uniform, and the contact resistance itself, when a remarkable pressure was needed and thickness was made thin, there was the same problem as a hotpress. In the fuel cell constituted by accumulating two or more cells, it will become what has difficult and low reliability to maintain fixed contact resistance over a long period of time by the stress relaxation of an electrode or a film, etc.

[0006]In order to solve these problems, on an electrode catalyst, the electrode preferably fabricated by the sheet shaped, or an electrode catalyst side, By carrying out spreading desiccation of the solution of solid polymer electrolyte resin, form a solid-electrolyte membrane directly and it is considered as a zygote, . [whether a solid-electrolyte membrane side is made to associate and the hotpress of the zygotes fabricated by carrying out in this way is carried out, and] Or. [whether a solvent is removed after making it associate after applying a solid polymer electrolyte resin solution or its solvent, and unifying, and] Or after making the thing which applied or dried [spreading] the solid polymer electrolyte solution to the inside of sheep dryness too at the electrode or the electrode surface after applying the solution of solid polymer electrolyte resin to an electrode surface associate, removing a solvent and considering it as the anode / film / negative pole integrally molded product is also proposed. However, in the method of applying a solid polymer electrolyte resin solution on an electrode catalyst layer side, and fabricating a film. Depending on electrode structure, film formability may have been bad, and needed to apply the solution too much, therefore osmosis of solid polymer electrolyte resin into an electrode catalyst layer may have become superfluous, and gas diffusion nature may have been checked. It was also difficult to consider it as uniform

thickness, and when it was going to make thickness thin, a possibility of producing an inter-electrode short circuit too was high.

[0007]The energy efficiency of the electrochemical device with which the polymers solid-electrolyte membrane was used for this invention, And it makes it possible to make thickness of a solid-electrolyte membrane thin that the operation with high current density should be made possible, And it aims at obtaining the electrode / film zygote, or the electrode / film / electrode conjugate which secures contact resistance with an electrode low and certainly, and does not necessarily need a heat pressing process, without spoiling the original physical properties of an electrode.

[0008]

[Means for Solving the Problem]According to this invention, a solid polymer electrolyte and an electrode conjugate forming in one a solid polymer electrolyte which consists of extension porosity polytetrafluoroethylene and solid polymer electrolyte resin contained in the porosity cavity part on the surface of an electrode to achieve the above objects are provided. It can be considered as the electrode / solid polymer electrolyte / electrode conjugate which formed an electrode in both sides of the above-mentioned solid polymer electrolyte at one.

[0009]Namely, by arranging an extension porosity polytetrafluoroethylene (PTFE) film on an electrode surface beforehand, when carrying out spreading film production of the solid polymer electrolyte resin solution on an electrode surface, Almost all pitches contain in a cavity part of extension porosity PTFE, and resin which permeated to a rear face in part contributes to junction as a binder with an electrode. Generally, in order to increase an electrode reaction point also inside an electrode, solid polymer electrolyte resin is contained in many cases, but bonding strength will become stronger in this case.

[0010]After same structure and an effect arrange that with which an extension porosity PTFE film was beforehand impregnated in a solid polymer electrolyte resin solution to an electrode surface, they are acquired also by removing a solvent. In this case, in order to prevent an extension porosity PTFE film and a solid polymer electrolyte resin compound film from solid electrolyte resin in an extension porosity PTFE film permeating an electrode too much, and becoming porosity (porous), Before arranging to an electrode surface, it is preferred to remove a solvent moderately beforehand, but if it removes too much, adhesive strength will decline, and resistance will become high.

[0011]For this reason, after an extension porosity PTFE film is beforehand impregnated in a solid electrolyte resin solution, After removing a solvent, forming an extension porosity PTFE film and a solid electrolyte resin compound film and applying a solid electrolyte resin solution to the surface or electrode surface as a binder anew, it is good to it also as a zygote to arrange on an electrode surface and remove a solvent after that under existence of a solvent. In joining the above solid polymer electrolyte and electrode, a solid polymer electrolyte solution can also

be beforehand applied slightly on the surface of an electrode material. This is effective in raising the adhesive property of a solid polymer electrolyte and an electrode.

[0012]On the other hand, same structure and an effect are acquired also in what formed an electrode beforehand on one side of extension porosity PTFE. Namely, although the solid polymer electrolyte resinous principle can permeate, Solid ingredients, such as catalyst powder, prepare an extension porosity PTFE film which has an aperture which cannot permeate, . [whether an ink-like thing or a paste state thing which has an ingredient which is an electrode formation ingredient, and which contains catalyst powder or electrode component powder, and solid polymer electrolyte resin at least is applied to the surface, and] Or by filtering a solution or dispersion liquid which has these ingredients, After removing a solvent or carrier fluid, such as a back these ink-like thing made to deposit on the surface, and forming an electrode in one side of extension porosity PTFE, it is good also as a zygote for a solid polymer electrolyte resin solution to be applied, impregnate with it further, from the rear face, remove a solvent, and form a polymers solid-electrolyte membrane.

[0013]After forming a polymers solid-electrolyte membrane beforehand conversely, structure of this invention and an effect can be acquired also by forming an electrode in the surface. Namely, either a thing which is in a semiarid condition by removing suitably a thing with which a solid polymer electrolyte resin solution was beforehand impregnated all over an opening of extension porosity PTFE, or its solvent, or a thing removed thoroughly is prepared, it can be considered as a zygote by applying the shape of ink or a paste state thing which changes from an electrode formation ingredient which contains a solid polymer electrolyte resinous principle at least to the surface, and removing a solvent. In this case, it is an indispensable condition that an electrode formation ingredient solution contains solid polymer electrolyte resin, since junction will become imperfect in not containing, it will be necessary to carry out heat braces further and, and sufficient performance will not be obtained, either.

[0014]Also in which method, even if structure of solid polymer electrolyte resin is stabilized and adhesive strength in particular does not apply press pressure by fully heating at temperature of 120 ° - about 180 ° after solvent removal, either, it will become sufficient. Of course, it is not required especially although heat pressing may be carried out further. Same method is applicable also to junction of a yin-and-yang pole. Namely. [whether an electrode / film zygote is prepared to the anode and each negative pole as mentioned above, and] yes -- a gap or the surface by the side of the film after preparing one side -- or after applying a solid polymer electrolyte solution to the surface of a counterelectrode which touches it in proper quantity as a binder, the anode / film / negative pole zygote, or the anode / film / film / negative pole zygote can be obtained by making it associate, and removing and heating a solvent. Of course, after preparing an electrode / film zygote, it is also possible to constitute an electrode / film / electrode from one process. That is, as following, it can carry out and an electrode / film /

electrode conjugate can also be manufactured.

[0015]** removing a solvent, after applying a solvent or a solution of solid polymer electrolyte resin to a solid polymer electrolyte side of an electrode / solid polymer electrolyte zygote and making the same electrode / solid polymer electrolyte zygote, or an electrode associate -- the -- carry out stress relief heat treatment.

** making the surface carry out being spreading impregnated of the solid polymer electrolyte resin solution, arranging the still more nearly same electrode / solid polymer electrolyte zygote, or electrode as the surface, and removing a solvent subsequently, after arranging an extension porosity PTFE film on an electrode -- the -- carry out stress relief heat treatment.

[0016]** removing a solvent, after arranging beforehand a film which carried out being spreading impregnated of the solid polymer electrolyte resin solution to a cavity part of extension porosity PTFE and arranging an electrode on the surface further on an electrode catalyst layer side -- the -- carry out stress relief heat treatment.

** A cavity part of an extension porosity PTFE film is beforehand impregnated in a solid polymer electrolyte resin solution, It heat-treats, after arranging an electrode to both sides of the compound electrolyte after preparing an extension porosity PTFE film and a solid polymer electrolyte resin-compound electrolyte which removed and obtained a solvent and applying a solvent or a solution of solid polymer electrolyte resin to the surface or electrode surface, and removing a solvent.

[0017]That with which a cavity part of an extension porosity PTFE film was beforehand impregnated in a solid polymer electrolyte resin solution like **** or **. Or although a solid polymer electrolyte solution was further applied after a thing which once removed a solvent from now on, or solvent removal, on both the surfaces. After applying paste state or an ink-like ingredient which has an electrode formation ingredient (for example, catalyst powder, solid polymer electrolyte resin, PTFE, or these mixtures), a solvent is removed and is heat-treated after that.

[0018]Thus, in the obtained electrode / film zygote, or the electrode / film / electrode conjugate. Since a solid polymer electrolyte is made to form directly on an electrode or it is joined on an electrode in the state with a still sufficient adhesive property after film formation, Since adhesion power with an electrode is high, and small junction of resistance is possible and an extension porosity PTFE film is used as a matrix of solid polymer electrolyte formation even if it does not perform heat pressing in particular etc., Also although it is called a porous electrode top, moreover, it can form in fixed thickness as a thin film certainly, and it can be considered as a film with high intensity. For example, prevention of a short circuit by creep of solid polymer electrolyte resin by compression at the time of heat pressing and a battery assembly, etc. or prevention of generating of dispersion in resistance can also be performed. Also when it is beforehand considered as extension porosity PTFE and solid polymer electrolyte bipolar

membrane, although an adhesive property still has polymer electrolyte resin including a solvent, only by it, there is no intensity and handling by the state, handling, is made possible. This has the same advantage, also when a resin solution is applied to the surface, and it became possible not to just obtain a zygote like this invention without combination with an extension porosity PTFE film.

[0019] Especially as an electrode used for this invention, it is not limited to the process, structure, etc., and if it is a thing which has a gestalt as an electrode, it can be used. Namely, a thing which pressed catalyst powder, PTFE, or powder mixture that added solid polymer electrolyte resin etc. further at this on charge collectors, such as ** carbon paper, a metal fiber nonwoven fabric, and a mesh. Although what carried out spreading shaping of the paste which has the same mixed ingredient as **** on a charge collector in a similar manner too, a thing which fabricated the same mixture as **** in the shape of a film by the cast etc., a thing which fabricated an ingredient to a sheet shaped by extrusion, roll pressure Nobu, or other means like ****, etc. are mentioned, It does not adhere to in particular this. As mentioned above still more conversely, after a solid polymer electrolyte is impregnated all over an opening of EPTFE, it may be what applied and formed in the surface a paste state thing or an ink-like thing which has the same mixed ingredient as **.

[0020] An extension porosity polytetrafluoroethylene (PTFE) film used for this invention is a porosity PTFE film which has the structure which consists of a microfilament which extends from minute tubercles and those minute tubercles of a large number produced by extension-porosity-izing a PTFE sheet, and connects both minute tubercles in three dimensions. As for thickness of an extension porosity PTFE film desirable to this invention, 1-100 micrometers of 0.5-2 micrometers and voidage of 3-30 micrometers and an aperture are 80 to 92% 60 to 98% preferably. [0.05-5 micrometers of] If thickness is too thin, it will become easy to generate a short circuit and gas leakage (cross leakage) too, if too thick, electrical resistance will become high, and an advantage by this invention is spoiled. If an aperture is too small, being impregnated of a solid polymer electrolyte will become difficult, if too large, holding power of a solid polymer electrolyte will become weak, and a reinforcing effect also becomes weak. If voidage is too small, resistance as a solid-electrolyte membrane will become large, if too large, generally intensity of the EPTFE itself will become weak and a reinforcing effect will not be acquired.

[0021] Various impalpable powder, such as ceramic powder, such as conductive powder, such as catalyst powder, such as platinum, carbon black, and black lead, and alumina, may be included in the range which electron conductivity furthermore does not produce in this extension porosity PTFE depending on the case. In this case, a homogeneous-mixing raw material in a primary particle level which is obtained by making coagglutinate after mixing dispersion after an emulsion polymerization of PTFE and dispersion liquid of these powder is

prepared, and the rest is obtained by processing it like said PTFE simple substance raw material.

[0022]Although various kinds of things can be used as solid polymer electrolyte resin according to a use, a polyethylene oxide alkali-metal-salt complex, a thing which carried out after-impregnating crosslinking treatment of this to extension porosity PTFE, etc. are mentioned, for example. Perphloro sulfonate resin is mentioned as a fuel cell, and this is sold by Du Pont as Nafion (registered trademark), and can be obtained as Nafion NR-50 as a solution. In addition, ion-exchange resin of various kinds of hydrocarbon systems and a fluorine system is used. A catalyst of platinum etc., carbon powder, and various ceramic powder may be added in the range which electron conductivity does not produce in this solid polymer electrolyte depending on the case.

[0023]Generally as a solvent of these resin solutions, an organic solvent of various hydrocarbon systems, water, or these partially aromatic solvents are used. What is necessary is for an extension porosity PTFE film to be hard to be impregnated depending on a molecular weight of resin, or a kind of solvent, when carrying out being spreading impregnated of the resin solution, but just to carry out suitably suitable processing of addition of concentration adjustment or a surface-active agent, a surface treatment of an extension porosity PTFE film, etc. in this case.

[0024]A solid polymer electrolyte and an electrode conjugate of this invention are shown in drawing 1 (A) and (B). As for a solid polymer electrolyte and 2, in the inside of drawing 1, and 1, an electrode and 3 are EPTFE(s) (a microfilament in a polymers solid-electrolyte membrane and 5 are solid polymer electrolytes a minute tubercle and 4.) in a polymers solid-electrolyte membrane. The mode which uses a solid polymer electrolyte and an electrode conjugate of this invention for various kinds of electrochemical devices can be the same as that of the conventional device.

[0025]An example of a fuel cell is shown in drawing 2. As for an electrode, and 7 and 8, a separator board, and 11 and 12 is [one] gas supplying grooves a charge collector, and 9 and 10 solid polymer electrolyte resin and PTFE bipolar membrane, and 2 and 3 among drawing 2. A solid polymer electrolyte and an electrode conjugate of this invention are used as a zygote of solid polymer electrolyte 1 / electrode 2, or a zygote of 2/of electrode solid polymer electrolyte 1 / electrode 3.

[0026]In this way, in a constituted polymers solid electrolyte fuel cell. If drawing 2 is referred to, O_2 will be supplied to the gas supplying groove 11 and H_2 will be supplied to the slot 12,

Within the electrode 2, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, A reaction of $2H_2 \rightarrow 4H^+ + 4e^-$ occurs within the electrode 3, $4H^+$ flows into the electrode 2 from the electrode 3 through the solid polymer electrolyte 1, and $4e^-$ becomes electrical energy by passing along external load. About 100 **

of operating temperature is about 80 °C preferably from 60 °C.

[0027]A solid polymer electrolyte and an electrode conjugate of this invention can be used for a water electrolysis system, an ozone generator besides a polymers solid electrolyte fuel cell, etc.

[0028]

[Example]

After applying the mixed solution of alkylene oxide polymer oligomer and chloric acid lithium which added the cross linking agent to the surface of the sheet shaped graphite electrode for lithium ion batteries which comprises PTFE 5% example 1 graphite 95%, 3 micrometers of thickness and extension porosity PTFE (Japan Gore-Tex make; Gore-Tex) of 93% of the void content were fixed to the surface, after carrying out being spreading impregnated of the same solution as having applied to the electrode from on the, it irradiated with the UV lamp, the bridge was constructed, and the electrode / electrolyte zygote was obtained.

[0029]After mixing solvent naphtha as a fluid lubrication agent example 2 carbon-black 65% into the mixture which comprises PTFE 35%, extrusion, While carrying out heating removal of the rolling sheet-sized back fluid lubrication agent, after extending 5 times and setting thickness to one fifth through a roll further, heating calcination was carried out at 350 °C, and 50 micrometers of thickness, 1 micrometer in the aperture, and the conductive breathable sheet of 78% of the void content were obtained. The gas diffusion layer which pastes up this sheet on carbon paper with a thickness of 0.2 mm which carried out Teflon impregnation treatment with a hotpress, and uses carbon paper as a charge collector was formed.

[0030]The ink-like solution which adds the back perphloro sulfonic acid resin solution which made IPA distribute the carbon black (it is henceforth considered as platinum carbon) which 25 % of the weight of platinum supported apart from this, distributes further, and is included at a rate of the perphloro sulfonate resin 30 to the platinum carbon 70 was prepared. After applying this solution on said gas diffusion layer, air-drying removed the solvent, the catalyst bed was formed, and the electrode of the polymers solid oxide fuel cell was produced. The amounts of platinum at this time were 0.3 mg / cm².

[0031]Next, it was air-dry, after fixing 20 micrometers of thickness, and the extension porosity PTFE sheet of 89% of voidage on the catalyst bed of this electrode and applying the perphloro sulfonic acid resin solution of 5% of concentration to that surface. The translucent film which repeated this spreading-air-drying 5 times and with which perphloro SURUFONSAN resin was filled up into the cavity part and the surface of the extension porosity PTFE film was formed. In this way, 130 °C of acquired Plastic solids were heated for 24 hours, and the zygote A of this invention was obtained.

[0032]After fixing four sides of the same extension porosity PTFE sheet as having used it in Example 2 of 15 micrometers of example 3 thickness, spreading impregnating desiccation of

the perphloro sulfonic acid resin solution of 5% of concentration was carried out. After ***** (ing) this 3 times and obtaining translucent extension porosity PTFE / perphloro sulfonic acid resin compound film thoroughly, The perphloro sulfonic acid resin solution was applied, after pasting up the electrode of the same polymers solid oxide fuel cell as having used it in Example 2 immediately after, the solvent was removed, 130 more ** was heated for 24 hours, and the zygote B of this invention was obtained.

[0033]Instead of finally applying a perphloro sulfonic acid resin solution in example 4 Example 3, IPA was applied to the electrode, extension porosity PTFE / perphloro sulfonic acid resin compound film was pasted immediately after, and also the zygote C of this invention was obtained similarly.

After preparing the two zygotes A produced in example 5 Example 2 and applying the perphloro sulfonic acid resin solution of 2% of concentration to the surface of the perphloro sulfonic acid resin layer of one sheet of them, After making the perphloro sulfonic acid resin layer side associate, and sticking two sheets by pressure so that air may not enter in between, and air-drying removing a solvent, 130 ** was heated for 24 hours and the electrode / film / film / electrode conjugate AA of this invention were obtained.

[0034]Used extension porosity PTFE of 30 micrometers of example 6 thickness, and also. After obtaining extension porosity PTFE / perphloro sulfonate resin like Example 3, the perphloro sulfonic acid resin solution of 2% of concentration is further applied to the both sides, Then, after it welded by pressure as it put by two electrodes of the same polymers solid electrolyte fuel cell as having used it in Example 2, and air-drying removed the solvent continuously, 130 ** was heated for 24 hours and the electrode / film / electrode conjugate of this invention were obtained.

[0035]After fixing extension porosity PTFE of 40 micrometers in thickness, and 92% of voidage on the same electrode of a polymers solid electrolyte fuel cell as having created in example 7 Example 2, spreading desiccation of the perphloro sulfonic acid resin solution of 5% of concentration was carried out. After repeating this 3 times, the electrode of one more sheet was welded by pressure, air-drying removed the solvent, without drying, after applying the 4th time, 130 ** was heated for 24 hours, and the electrode / film / electrode conjugate of this invention were obtained.

[0036]supplying the hydrogen humidified on the one side using the zygote AA obtained in example 8 Example 5 – already – oxygen was supplied to the field of the method of one, and when it was made to operate as a fuel cell under 80 ** heating, the performance of 0.78V was obtained by $1\text{A}/\text{cm}^2$.

[0037]

[Effect of the Invention]According to the solid polymer electrolyte and the electrode conjugate which formed in the surface of an electrode of this invention at one the solid polymer

electrolyte which consists of extension porosity PTFE and solid polymer electrolyte resin contained in the porosity cavity part. Since thickness of a polymers solid-electrolyte membrane can be made thin, it is possible to raise the energy efficiency and current density of an electrochemical device, without not necessarily needing a heat pressing process, securing contact resistance with an electrode low, without spoiling the physical properties of an electrode.

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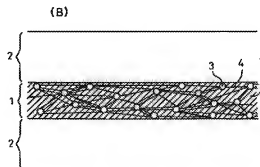
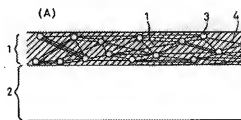
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(54) 【発明の名称】 高分子固体電解質・電極接合体

(57) 【要約】

【目的】 電極の物性を損なうことなく、電極との接触部抗を低く確保しながら、高分子固体電解質膜の厚さを薄くして電気化学装置のエネルギー効率及び電流密度を向上させること。

【構成】 電極の表面に、延伸多孔質ポリテトラフルオロエチレンとその多孔質空隙部に含有された高分子固体電解質樹脂とからなる高分子固体電解質を一体に形成した高分子固体電解質・電極接合体。上記の高分子固体電解質の両面に電極を一体に形成してもよい。



【特許請求の範囲】

【請求項1】 電極の表面に、延伸多孔質ポリテトラフルオロエチレンとその多孔質空隙部に含有された高分子固体電解質樹脂とからなる高分子固体電解質を一体に形成したことを特徴とする高分子固体電解質・電極接合体。

【請求項2】 前記高分子固体電解質の両面に電極を一体に形成したことを特徴とする請求項1記載の高分子固体電解質・電極接合体。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は高分子固体電解質・電極接合体に係わる。より詳しくは、イオン導電性高分子固体電解質を使用する電気化学装置の電極・高分子固体電解質接合体に係わり、例えば、リチウムイオン伝導性固体電解質を使用したリチウム電池或いはプロトン伝導性固体電解質を使用した水電解装置等に利用し得るが、最速にはプロトン伝導性固体電解質を使用する高分子固体電解質型燃料電池に使用することである。

【0002】

【従来の技術】 高分子固体電解質を使用した電気化学装置ではエネルギー効率の一層の向上が求められており、そのため電極構造を工夫し、電極反応点を三次元化して反応活性点を増やすとともに高分子固体電解質を電極内部にも浸透し、速やかにイオンが移動できる様にしていく。発生したイオンを速やかに対極まで移動できる様にするためには、電極内の固体電解質と隙間である固体電解質膜との接触が良く、又固体電解質膜自体の膜抵抗が低い必要があり、そのためには膜厚はできるだけ薄い方が好ましい。更に、燃料電池で使用されている高分子固体電解質膜は常に湿潤状態で使用しなければイオン伝導性の低下や、分解が発生して性能が低下するため、反応ガスに加湿して、間接的に湿潤状態を維持するようにしているが、高分子固体電解質膜が薄いほど加湿効率が悪く、限界電流密度の向上が期待できる。

【0003】 また、従来は、固体電解質膜と電極をそれぞれ別に用意し、これらを重ね合わせた後ホットプレスにより接合する方法が一般的に行われており、高分子固体電解質としては市販品として限定的に形成されたもの（例えば東洋デュポン社ナフイオン#115等）や、その溶液をキャストして薄膜状に形成したもの等が使用されている。またホットプレスせずに機械的にはさみこんで使用することも提案されている。

【0004】

【発明が解決しようとする課題】 しかしながら、ホットプレスによる接合に於いては、温度により膜が軟化したところで圧力が加えられたため、膜厚をあまり薄くすると膜が破断されて、ガス漏れを生じたり、電極間の短絡が発生したりしやすいという問題があった。このことは電極の平滑性が高いときには更に難しい問題となった

め、極端に膜厚を薄くすることは困難であった。またホットプレス時に電極自体も圧密化されるため、高電流密度での作動を可能にするための電極の重要な要素である通気性を損なうという問題もあった。

【0005】 これら等の問題を解決し、またホットプレス工程そのものを省略できるということで、機械的にはさみこんで使用する方も提案されているが、電極との接触を一樣に保つこと及び界面抵抗自体を低く保つためには、かなりの圧力を必要とし、膜厚を薄くした場合、ホットプレスと同様の問題があった。また複数セルを積み重ねて構成される燃料電池に於いては、電極または膜の応力緩和等により長期にわたって一定の接触抵抗を保つことは困難であり信頼性の低いものになってしまう。

【0006】 これらの問題を解決する為、電極触媒、好ましくはシート状に成形された電極または電極触媒膜上に、高分子固体電解質樹脂の溶液を塗布乾燥することにより直接固体電解質膜を形成して接合体とし、更にこの様にして成形された接合体どうしを固体電解質膜面をつき合わせてホットプレスするか、または高分子固体電解質樹脂溶液またはその溶液を塗布した後をつき合わせて一体化した後溶媒を除去するか、または電極面に高分子固体電解質樹脂の溶液を塗布した後乾燥状態のうちにやはり電極または電極面に高分子固体電解質溶液を塗布または塗布乾燥したものをつき合わせた後、溶媒を除去して膜抵抗/膜厚/陰極一体成形品とすることも提案されている。しかしながら、電極触媒膜面上に高分子固体電解質樹脂溶液を塗布して膜を成形する方法では、電極構造によっては造膜性が悪く、過度に溶液を塗布する必要があり、そのため電極触媒膜内への高分子固体電解質樹脂の浸透が過剰になり、ガス拡散性を阻害する可能性がある。また均一な膜厚とすることも難しく、膜厚を薄くしようとする場合、やはり電極間の短絡を生じる可能性が高いものであった。

【0007】 本発明は、高分子固体電解質膜を使用した電気化学装置のエネルギー効率、及び高電流密度での作動を可能とすべく、固体電解質膜の厚さを薄くすることを可能とし、しかも電極本来の物性を損なわずに、電極との接触抵抗を低く且つ確実に確保し、また必ずしもホットプレス工程を必要としない電極/膜接合体または電極/膜/膜接合体を得ることを目的とする。

【0008】

【課題を解決するための手段】 本発明によれば、上記目的を達成するために、電極の表面に、延伸多孔質ポリテトラフルオロエチレンとその多孔質空隙部に含有された高分子固体電解質樹脂とからなる高分子固体電解質を一体に形成したことを特徴とする高分子固体電解質・電極接合体を提供する。また、上記の高分子固体電解質の両面に電極を一体に形成した電極/高分子固体電解質/電極接合体とすることができ、

【0009】 即ち、電極面上に高分子固体電解質樹脂溶

液を塗布膜製する際、延伸多孔質ポリテトラフルオロエチレン（PTFE）フィルムを予め電極面上に配置しておくことにより、殆どの樹脂成分が延伸多孔質PTFEの空隙部に含有され、一部表面まで浸透した樹脂が電極とのバインダーとして接合に寄与する。一般的には、電極内部にも電極反応点を増やすために高分子固体電解質樹脂が含まれることが多いが、この場合には接合強度はより強いものとなる。

【0010】同様の構造及び効果は延伸多孔質PTFE膜に予め高分子固体電解質樹脂溶液を含浸したものを電極面に配置した後に、溶媒を除去することによっても得られる。この場合、延伸多孔質PTFE膜内の固体電解質樹脂が電極に透過してしまい延伸多孔質PTFE膜・高分子固体電解質樹脂複合膜が多孔質（ポーラス）になってしまうことを防止するために、電極面に配置する前に予め適度に溶媒を除去しておくことが好ましいが、除去しすぎると接着力が低下し、抵抗が高くなってしまう。

【0011】このため予め延伸多孔質PTFE膜に固体電解質樹脂溶液を含浸した後、溶媒を除去して延伸多孔質PTFE膜・固体電解質樹脂複合膜を形成した後、改めてバインダーとして固体電解質樹脂溶液をその表面または電極面に塗布した後、溶媒の存在下に電極面上に配置し、その後溶媒を除去して複合体としてもよい。以上の高分子固体電解質と電極とを混合するに当って、電極材料の表面に予め高分子固体電解質溶液をわずかに塗布しておくこともできる。これは高分子固体電解質と電極との接着性を向上させる効果がある。

【0012】一方、延伸多孔質PTFEの片面上に予め電極を形成しておいたものにおいても、同様の構造及び効果が得られる。すなわち高分子固体電解質樹脂成分は浸透できるが、触媒粉末等の固体成分は浸透出来ないような孔徑を有する延伸多孔質PTFE膜を用い、その表面に電極形成成分である少なくとも触媒粉末或いは電極形成粉末及び高分子固体電解質樹脂を含む成分を有するインク状物またはペースト状物を塗布するか、またはこれら成分を有する溶媒または分散液を塗布することにより、表面に堆積させた後これらインク状物等の溶媒または分散液を除去して、延伸多孔質PTFEの片面に電極を形成した後、その表面から更に高分子固体電解質樹脂溶液を塗布、含浸させ、溶媒を除去して高分子固体電解質膜を形成して複合体としてもよい。

【0013】また逆に高分子固体電解質膜を予め形成した後、その表面に電極を形成することによっても本発明の構造、効果を得ることができる。すなわち、延伸多孔質PTFEの空隙中に予め高分子固体電解質樹脂溶液を含浸したものの或いはその溶媒を適当に除去することにより半乾燥状態にあるもの或いは完全に除去したもののいずれかを用意し、その表面に、少なくとも高分子固体電解質樹脂成分を含む電極形成成分から成るインク状た

はペースト状物を塗布し、溶媒を除去することにより複合体とすることができる。この場合、電極形成成分が高分子固体電解質樹脂を含むことが必須条件であり、含まない場合には複合体は不完全なものとなるため、さらにヒートプレスする必要があるが生じてしまい、また充分な性能も得られない。

【0014】いずれの方法においても、溶媒除去後に120℃～180℃程度の温度で十分に加熱することにより高分子固体電解質樹脂の構造が安定し、接着力も特にプレス圧をかけなくても十分なものとなる。勿論、さらにヒートプレスしてもよいが特に必要ではない。更に、陰陽極の接合に対しても同様の方法が適用できる。即ち、前記のようにして電極/陰極複合体を陽極、陰極それぞれに対して堆積するか、又はいずれか一方を準備した後、その膜側の表面かまたはそれと接する対向電極の表面に高分子固体電解質溶液をバインダーとして塗布させた後、つき合わせ、溶剤を除去し、加熱することにより陰極/膜/陰極複合体または陽極/膜/膜/陰極複合体を得ることができる。勿論、電極/膜複合体を準備した後ではなく、電極/膜/電極を二工程で構成することも可能である。即ち、下記の如くして電極/膜/電極複合体を製造することもできる。

【0015】① 電極/高分子固体電解質複合体の高分子固体電解質面に高分子固体電解質樹脂の溶媒または溶媒を塗布し、同様の電極/高分子固体電解質複合体または電極をつき合わせた後、溶媒を除去し、その後熱処理する。

② 電極上に延伸多孔質PTFE膜を配置した後、その表面に高分子固体電解質樹脂溶液を塗布含浸させ、さらにその表面に陽極の電極/高分子固体電解質複合体または電極を配置し、次いで溶媒を除去し、その後熱処理する。

【0016】③ 電極触媒膜面上に、予め延伸多孔質PTFEの空隙部に高分子固体電解質樹脂溶液を塗布含浸させた膜を配置し、さらにその表面に電極を配置した後溶媒を除去し、その後熱処理する。

④ 予め延伸多孔質PTFE膜の空隙部に高分子固体電解質樹脂溶液を含浸し、溶媒を除去して得た延伸多孔質PTFE膜・高分子固体電解質樹脂複合電解質を用意し、その表面または電極面に高分子固体電解質樹脂の溶媒または溶媒を塗布した後、その複合電解質の両面に電極を配置し、溶媒を除去した後、熱処理する。

【0017】⑤ または④と同様に予め延伸多孔質PTFE膜の空隙部に高分子固体電解質樹脂溶液を含浸したもの、或いはこれから一旦溶媒を除去したもの、或いは溶媒除去後に高分子固体電解質樹脂溶液を塗布したものの膜表面に、電極形成成分（例えば触媒粉末と高分子固体電解質樹脂またはPTFEまたはこれらの混合物）を有するペースト状またはインク状成分を塗布後に、溶媒を除去し、その後熱処理する。

【0018】このようにして得た電極/接合体または電極/膜/電極接合体では、電極上で直接に高分子固体電解質を形成させるか、または膜形成後の未だ接着性のよい状態の電極上に接合されるため、特にヒートプレスなどを行わなくても電極との密着力が高く、抵抗の小さい接合が可能であり、また延伸多孔質PTFE膜を高分子固体電解質形成のマトリックスとして使用しているために、多孔質の電極上といえども確実に一定の膜厚にしかも薄膜として形成することができ、また強度の高い膜とすることができる。さらに、例えば、ヒートプレス時や電池組立時の圧縮等による高分子固体電解質樹脂のクランプによる短絡の防止あるいは抵抗のばらつき等の発生の防止もできる。また予め延伸多孔質PTFE・高分子固体電解質複合膜とした場合にも、高分子固体電解質樹脂が未だ溶融を含み、接着性があるがそれのみでは強度がなく、取扱いできない状態での取扱を可能にする。このことは表面に樹脂溶液を塗布した場合にも同様の利点があり、まさに延伸多孔質PTFE膜との組合せにより初めて本発明のような接合体を得ることが可能になったのである。

【0019】本発明に用いる電極としては、その製法、構造等に特に限定されるものではなく、電極としての形態を有する物であれば使用し得る。すなわち①カーボンペーパー、金属繊維複合膜、メッシュ等の集電体上に、触媒粉末とPTFE、またはこれに更に高分子固体電解質樹脂等を加えた混合粉末をプレスしたもの、②、③と同様の混合成分を有するペーストをやはり同集電体上に塗布成形したもの、④、⑤と同様の混合物をキャスト等により膜状に成形したもの、⑥、⑦と同様の成分を押出またはロール圧延等の手段によりシート状に成形したものなどが挙げられるが、特にこれにこだわるものではない。さらに逆に、前述したようにEPTFEの空腔中に高分子固体電解質を含浸した後、その表面に⑥と同様の混合成分を有するペースト状物あるいはインク状物を塗布して形成した膜なものであってもよい。

【0020】本発明に使用する延伸多孔質ポリテトラフルオロエチレン（PTFE）膜はPTFEシートを延伸多孔質化して得られる、多量の微小結節とそれらの微小結節から延出して微小結節相互を三次元的に連結する微細繊維とからなる構造を有する多孔質PTFE膜である。本発明に好ましい延伸多孔質PTFE膜の厚度は $1 \sim 100 \mu\text{m}$ 、好ましくは $3 \sim 90 \mu\text{m}$ 、孔径は $0.05 \sim 5 \mu\text{m}$ 、好ましくは $0.5 \sim 2 \mu\text{m}$ 、空隙率は $60 \sim 98\%$ 、好ましくは $80 \sim 92\%$ である。膜厚が薄すぎるとやはり短絡や、ガス漏れ（クロスリーク）が発生しやすくなり、厚すぎると電気抵抗が高くなり、本発明による利点が損なわれる。孔径が小さすぎると高分子固体電解質の含浸が困難となり、大きすぎると高分子固体電解質の保持力が弱くなり、また補強効果も弱くなる。空隙率が小さすぎると固体電解質浸透時の抵抗が大きくな

り、大きすぎると一般にEPTFE自体の強度が弱くなり補強効果が得られない。

【0021】さらに場合によっては、この延伸多孔質PTFEに電子伝導性の生じない範囲で白金などの触媒、炭素粉、カーボンブラック、黒鉛等の導電性粉末、アルミナ等のセラミック粉等の各種微粉末を含ませてもよい。この場合には、PTFEの粒子化重合後のディスパーションとこれら粉末の分散液を混合後、共凝集させて得られる様な一次粒子レベルでの均一混合原料を用意し、あとは前記PTFE単体原料と同様に加工することによって得られる。

【0022】高分子固体電解質樹脂としては、用途に応じて各種のものが使用できるが、例えば、ポリエチレンオキサイド-アルカリ金属塩複合体や、これを延伸多孔質PTFEに含浸後架橋処理したものなどが挙げられる。また燃料電池としてはパーフルオロスルホン酸樹脂が挙げられ、これはデュポン社よりナフィオン（登録商標）として販売されており、溶液としてはナフィオンN R-50として入手できる。そのほか各種の炭化水素系、フッ素系のイオン交換樹脂が用いられる。また場合によってはこの高分子固体電解質に、電子導電性の生じない範囲で白金などの触媒やカーボン粉末、各種セラミックス粉末を加えてもよい。

【0023】これは樹脂溶液の溶媒としては一般に各種炭化水素系の有機溶剤、水、あるいはこれらの混合溶剤が使用される。延伸多孔質PTFE膜に樹脂溶液を塗布含浸する場合、樹脂の分子量や溶媒の価数によっては含浸しにくいことがあるが、この場合、濃度調整や界面活性剤の添加、延伸多孔質PTFE膜の表面処理など、適宜適切な処理をすればよい。

【0024】図1（A）（B）に本発明の高分子固体電解質・電極接合体を示す。図1中、1は高分子固体電解質、2は電極、3は高分子固体電解質膜内のEPTFEの（微小結節、4は高分子固体電解質膜内の微細繊維、5は高分子固体電解質である。本発明の高分子固体電解質・電極接合体を各種の電気化学装置に使用する態様は従来の装置と同様であることができる。

【0025】図2に燃料電池の例を示す。図2中、1は高分子固体電解質樹脂・PTFE複合膜、2、3は電極、7、8は集電体、9、10はセパレーティング板、11、12はガス供給槽である。高分子固体電解質1/電極2の接合体又は電極2/高分子固体電解質1/電極3の接合体として本発明の高分子固体電解質・電極接合体を使用する。

【0026】こうして構成された高分子固体電解質燃料電池では、図2を参照すると、ガス供給槽11に O_2 を槽12に H_2 を供給すると、電極2内で $\text{O}_2 + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$ 、電極3内で $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$ の反応が起こり、 4H^+ は高分子固体電解質1を通過して電極3から電極2へ流れ、 4e^- は外部負荷を流ること

により電気エネルギーとなる。作動温度は0℃から100℃程度、好ましくは80℃程度である。

【0027】なお、本発明の高分子固体電解質・電極接合体は高分子固体電解質原料電池のほか、水電解装置やオゾン発生器などにも使用できる。

【0028】

【実施例】

実施例1

グラファイト95%、PTFE5%から成るシート状のリチウムイオン電池用黒鉛電極の表面に架橋剤を加えたアルキレンオキサイド重合体オリゴマー及び塩素酸リチウムの混合溶液を塗布した後、膜厚3μm、空孔率93%の延伸多孔質PTFE（ジャンゴアテックス製；ゴアテックス）をその表面に固定し、その上から電極に塗布したのと同じ溶液を塗布浸漬した後UVランプを照射し架橋して電極/電解質接合体を得た。

【0029】実施例2

カーボンブラック85%、PTFE15%から成る混合物に液状溶剤としてのジメチルベンゼンを混合した後押出、圧延シート化後液状溶剤を加熱除去すると同時に5倍に延伸し、さらにロールを通して膜厚を1/5にした後350℃で加熱乾燥して、膜厚50μm、孔径1μm、空孔率78%の導電性通気性シートを得た。このシートをテフロン浸漬処理をした厚さ0.2mmのカーボンペーパーにホットプレスにより接着して、カーボンペーパーを集電体とする、ガム拉膜を形成した。

【0030】これとは別に、白金25重量%担持したカーボンブラック（以後白金カーボンとする）を1PAに分散させたパーフロスルフォン酸樹脂溶液を加え更に分散させて白金カーボン70に対しパーフロスルフォン酸樹脂30の割合で含む、インク状溶液を準備した。この溶液を前記ガス拡散層の上に塗布した後、溶液を風乾により除去して触媒層を形成して高分子固体電解質原料電池の電極を製作した。この時の白金量は0.3mg/cm²であった。

【0031】次に、この電極の触媒層の上に膜厚20μm、空孔率89%の延伸多孔質PTFEシートを固定した後その表面に濃度5%のパーフロスルフォン酸樹脂溶液を塗布した後風乾した。この塗布—風乾を5回繰り返して、延伸多孔質PTFEの空隙部及び表面にパーフロスルフォン酸樹脂が充填された、半透明の膜を形成した。こうして得られた成形体を130℃24時間加熱して本発明の接合体Aを得た。

【0032】実施例3

膜厚15μmの実施例2で使したのと同じ延伸多孔質PTFEシートの4辺を固定した後、濃度5%のパーフロスルフォン酸樹脂溶液を塗布含浸乾燥した。これを3回くりかえて、完全に半透明の延伸多孔質PTFE/パーフロスルフォン酸樹脂接合体を得た後、更にパーフロスルフォン酸樹脂溶液を塗布し、直後に実施例

2で使したのと同じ高分子固体電解質原料電池の電極を接着した後溶媒を除去し、さらに130℃24時間加熱して本発明の接合体Bを得た。

【0033】実施例4

実施例3に於いて最後にパーフロスルフォン酸樹脂溶液を塗布する代わりに、電極にIPAを塗布し、直後に延伸多孔質PTFE/パーフロスルフォン酸樹脂接合体に接着した他は同様に本発明の接合体Cを得た。

実施例5

実施例2で作製した接合体Aを2枚用意し、その内の1枚のパーフロスルフォン酸樹脂膜の表面に濃度2%のパーフロスルフォン酸樹脂溶液を塗布した後、間に空気の入らないように2枚をパーフロスルフォン酸樹脂膜面をつき合わせて圧着し、風乾により溶剤を除去した後130℃24時間加熱して本発明の電極/膜/電極接合体Aを得た。

【0034】実施例6

膜厚30μmの延伸多孔質PTFEを使用した他は、実施例3と同様に延伸多孔質PTFE/パーフロスルフォン酸樹脂を得た後更にその両面に濃度2%のパーフロスルフォン酸樹脂溶液を塗布し、続いて実施例2で使したのと同じ高分子固体電解質原料電池の電極2枚で挟み込むようにして圧接し、乾いて風乾により溶剤を除去した後、130℃24時間加熱して、本発明の電極/膜/電極接合体を得た。

【0035】実施例7

実施例2で作成したのと同じ高分子固体電解質原料電池の電極の上に、厚さ40μm、空孔率92%の延伸多孔質PTFEを固定した後、濃度5%のパーフロスルフォン酸樹脂溶液を塗布乾燥した。これを3回繰り返した後、4回目を塗布した後乾燥せずに、もう1枚の電極を圧接し、風乾により溶剤を除去し、130℃24時間加熱して本発明の電極/膜/電極接合体を得た。

【0036】実施例8

実施例5で得た接合体Aを使用してその片面に加熱した水素を供給し、もう1方の面に酸素を供給し、80℃加熱下で燃料電池として作動させたところ1A/cm²で0.78Vの性能が得られた。

【0037】

【発明の効果】本発明の、電極の表面に、延伸多孔質PTFEとその多孔質空隙部に含有された高分子固体電解質樹脂とからなる高分子固体電解質を一体に形成した高分子固体電解質・電極接合体によれば、電極の物性を損なうことなく、電極との接触抵抗を低く確保しながら、かつ必ずしもヒートプレス工程を必要としないで、高分子固体電解質原料の厚さを薄くすることができるので、電気化学装置のエネルギー効率及び電流密度を向上させることが可能である。

【図面の簡単な説明】

【図1】本発明の実施例の高分子固体電解質/電極接合

体 (A) 及び電極／高分子固体電解質／電極接合体 (B) の断面図である。

【図 2】 燃料電池の例を示す断面図である。

【符号の説明】

1…高分子固体電解質複合膜

2, 3…電極

4…微小結節

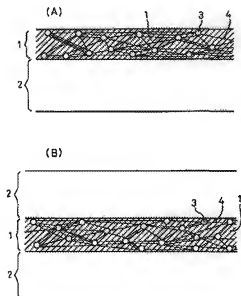
5…微細繊維

7, 8…集電体

9, 10…セパレータ

11, 12…ガス供給溝

【図 1】



【図 2】

